

A New Polymorph of Eucryptite (LiAlSiO_4) and Thermal Expansion of α and ϵ Eucryptite at High Pressure

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Introduction: The hexagonal aluminosilicate β -eucryptite (LiAlSiO_4) has been of continuing interest to mineralogists due to its structural similarity to quartz¹ (i.e., half of the $[\text{SiO}_4]^{4-}$ tetrahedra in quartz are replaced by $[\text{AlO}_4]^{5-}$ tetrahedra and the charge is balanced by the incorporation of Li^+ into the main structural channels parallel to the c axis). Of particular significance to the field of material sciences is its unusual thermal-expansion properties observed at ambient pressure. As already demonstrated by many experimental studies, expansion within the (001) plane of the structure is approximately canceled by contraction along the c axis, yielding negative thermal expansion along the c axis ($\alpha_c \approx -2\alpha_a$) and near-zero volume thermal expansion over a wide temperature range of 300-1400 K². The initial objective of this study was to examine whether these remarkable thermal-expansion properties in β -eucryptite persist at elevated pressures.

Methods and Materials: The starting β -eucryptite sample was synthesized from Li_2CO_3 , Al_2O_3 , and $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ powders in the molar ratio 1:1:2. The mixture was first sintered at 1373 K for 15 hours and, after regrinding, resintered at 1573 K for 24 hours. X-ray diffraction experiments were performed using the DIA-type and large-volume apparatus. An energy-dispersive X-ray method was employed using white radiation from the superconducting wiggler magnet at Beamline X17B of the National Synchrotron Light Source. The incident X-ray beam was collimated to dimensions of $100 \times 200 \mu\text{m}$, and diffracted X-rays were collected by a solid-state Ge detector at fixed angles of 2θ ($\approx 7.4^\circ$). Pressure was determined by EOS of NaCl and temperature by a W-Re thermocouple. In the room-temperature experiment of exploring the reversibility of the transformation between β and ϵ eucryptite, the data were collected at steps of 0.3-0.4 GPa. In the high P and T experiment, the sample was first compressed at room temperature to 2.2 GPa, followed by heating to the maximum temperature of 1073 K. On cooling, the pressure was controlled to be constant within 0.05 GPa of the desired value at each temperature condition. X-ray diffraction data were collected on both heating and cooling, at steps of 50-100 K.

Results: During compression at room temperature, β -eucryptite destabilized and underwent a polymorphic phase transformation to a previously undescribed phase. We were therefore unable to study the thermal expansion of β -eucryptite at high pressure. The novel transition is reversible and first-order in character. The new phase, referred to here as ϵ -eucryptite, can be indexed according to an orthorhombic unit cell with $a = 10.217(4) \text{ \AA}$, $b = 8.487(4) \text{ \AA}$, $c = 5.751(3) \text{ \AA}$, and $V = 498.7(4) \text{ \AA}^3$ at 2.2 GPa and 298 K. On heating at 2.2 GPa, ϵ -eucryptite and β -eucryptite were metastable over the temperature interval 298-873 K; at higher temperatures they underwent an irreversible phase transition to α -eucryptite. Both α -eucryptite and ϵ -eucryptite show anisotropic thermal expansion along different crystallographic axes. For α -eucryptite, we obtain $\alpha_a = 6.71(\pm 0.25) \times 10^{-6} \text{ K}^{-1}$, $\alpha_c = 1.07(\pm 0.05) \times 10^{-5} \text{ K}^{-1}$, and $\alpha_v = 2.42(\pm 0.1) \times 10^{-5} \text{ K}^{-1}$ at 1.94(2) GPa over the temperature range 298-1073 K. For ϵ -eucryptite at 2.32(8) GPa, we find larger thermal expansion in a smaller temperature range 298-773 K, with $\alpha_a = 1.47(\pm 0.15) \times 10^{-5} \text{ K}^{-1}$, $\alpha_b = 6.65(\pm 1.33) \times 10^{-6} \text{ K}^{-1}$, $\alpha_c = 7.83(\pm 0.88) \times 10^{-6} \text{ K}^{-1}$, and $\alpha_v = 2.99(\pm 0.15) \times 10^{-5} \text{ K}^{-1}$. In combination with a previous determination of thermal expansion at ambient pressure³, the pressure effect on volume thermal expansion of α -eucryptite is determined to be $-2.68 \times 10^{-6} \text{ GPa}^{-1} \text{ K}^{-1}$, and the temperature derivative of the bulk modulus is estimated to be $-0.015 \text{ GPa K}^{-1}$. These results provide important parameters for the phase equilibrium calculations in the system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$.

Conclusions: Our experimental study demonstrates that β -eucryptite undergoes a novel, reversible phase transformation to ϵ -eucryptite on room-temperature compression. The P-V-T measurements on α -eucryptite provide important EOS parameters for the phase equilibrium calculations in the system $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$.

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